RAW MATERIALS

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FELDSPAR MATERIALS IN UKRAINE

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The possibility of use of complex types of feldspar raw material by ceramics plants is examined. The characteristics of the chemical composition of the basic geological-industrial types of feldspar raw material deposits in Ukraine are presented.

Key words: nonplastic ceramic materials, feldspars, pegmatites.

The nonplastic materials used in the ceramics plant are divided into grog (quartz sand, cullet of sintered articles, fireclay) and fluxes. Feldspar materials which act as grog components in the first stages of porcelain formation and as fluxes that cause formation of a glassy phase when the softening point is attained (1150 – 1350°C) act as a universal flux in ceramics technology and production of glazes and enamels.

The largest feldspar reserves, 337 million tons, represented by feldspar sands, have been proven in Belarus. In second place are the feldspar reserves in Russia, estimated at 115 million tons. With respect to the total feldspar reserves, basically represented by pegmatites and microgranodiorites (porcelain stones), a total of approximately 9 million tons, Ukraine is in sixth place in the world, while it is only 39th for extraction [1].

The demand for quality feldspar raw material is relatively high in Ukraine, more than 50,000 tons a year. However, despite the important potential, the country is experiencing a shortage of high-quality potassium feldspars whose main composition requirements are: minimum of 8 – 12% alkali metal oxide content, 0.15 – 0.20% iron oxide content for brands used in production of household porcelain (up to 0.30% for rocks used in production of electrotechnical porcelain), minimum amount of alkaline-earth element compounds and other harmful impurities. The potassium ratio (K_2O/Na_2O) of feldspars should be a minimum of 2 (greater than 3 for high-quality potassium feldspars) [2].

To satisfy the requirements of industry, feldspar raw material is supplied by Russia, Uzbekistan, Kazakhstan, and other countries. Less than 15% of the demand is covered by its own raw material even though the cost of feldspar raw material mined in Ukraine is 2 – 6 times less than for imported feldspar.

The mined raw materials are usually sold in unconcentrated form so that their price on external markets is low. For example, the price of feldspar raw material is \$15 – 20 per ton, and the cost of clay is \$25 – 40 per ton. For comparison, we note that the finished raw material concentrated by foreign firms and mixtures for elite ceramics cost \$150 a ton. At the same time, imported raw material intermediate products are used in practice by many ceramics enterprises.

According to one of the many classifications of pegmatites on which the ore-mineral, textural, paragenetic, mineral, and geochemical traits are based, pegmatites of the Ukrainian shield delimited by the raised southwestern part of the Eastern European platform bed are divided into six formations and subformations: rare-metal, rare-metal–mica-bearing, rare-metal–rare-earth, rare-earth, mica-bearing–ceramic, and crystal-bearing [3]. As a function of the content of the basic ore minerals, overall mineral composition, and geochemical characterization, each of these formations is divided into several types and subtypes. The mica-bearing–ceramic formation is the most widespread among pegmatites.

The pegmatites of this formation belong to the calcium-sodium-potassium geochemical subtype. The relative significance of alkali metal oxides in them is usually low and is related to the amount of mica in them.

The average chemical composition of Ukrainian pegmatites is represented by the following data (%):[2] 70.66 – 77.59 SiO_2; 13.26 – 17.15 Al_2O_3; 0.26 – 0.81 Fe_2O_3;

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[2] Here and below — content by weight.

0.50 – 1.32 CaO; 0.19 – 0.40 MgO; 3.02 – 6.80 K_2O; 2.36 – 5.35 Na_2O; the K_2O:Na_2O ratio is 0.6 – 1.8. The drawbacks of pegmatite raw material include the presence of impurities of iron minerals, biotite and magnetite, which contaminate the melt with dark spallings, as well as a low potassium ratio.

Volyn' and Priazov'e pegmatites are the basic source of feldspar ceramic raw material in Ukraine. The location of 14 and 19 pegmatite fields has been identified in these regions. The most valuable raw material for manufacture of high-quality potassium and sodium feldspars is represented by granitic pegmatites whose deposits are being worked in the following regions: Zhitomir (Polonno-Baranovskoe, Malinskoe, Zhitomirskoe, Gruzlivetskoe, etc.), Zaporozhe (Eliseevskoe, Gulyai-Pol'skoe, Andreevskoe, etc.), Rovno (Bil'chakovskoe, Koretskoe, Gorodnitskoe, etc.), Donetsk (Krasnovskoe, Anadol'skoe), and Khmelnitsky (Maidano-Labunovskoe).

The pegmatites whose fields are located in the Western Priazov'e have been studied in the most detail. They include the Eliseevskoe bed whose projected reserves are 20 million tons. This means that the total projected reserves of quartz-feldspar raw material in the Eliseevskoe field located in the Zaporozhe Oblast' can meet the requirements of Ukraine for the examined type of raw material for hundreds of years. The largest of the proven beds in this field are: Balka Velikogo Tabora, Dal'nyaya Kamchatka, Balka Glubokaya, and Dolinskoe.

The only pegmatite bed currently being worked is Balka Velikogo Tabora, whose total raw material reserves are 7.0 million tons, approximately 80% of all proven ceramic pegmatite reserves in Ukraine. The composition of the pegmatites in this bed is qualified as microcline-oligoclase-albite, where pegmatites of microcline and orthoclase compositions are less developed in the rock. Together with quartz, feldspars constitute up to 90% of the volume of the rock. Muscovite, biotite, garnet, tourmaline, apatite, and magnetite are present in the amount of 1 to 10%. Approximately 50 minerals, including uranium minerals, are found as traces [4]. The pegmatite in this bed is not subject to concentration.

The Andreevskoe pegmatite field (Donetsk Oblast') is represented by the Kamennaya Skala (microcline type) and Krasnaya Gora beds, whose basic rocks are amphibole gneisses and amphibolites of the western Priazov'e series.

The Polonno-Baranovskoe pegmatite field is located in the Volyn Oblast'. Several sections traditionally used by the Volyn porcelain industry as local feldspar raw material have been distinguished within the boundaries of the field. The pegmatite material in the bed has a block occurrence. The blocks consist of granite, potassium feldspar, oligoclase or albite, quartz, and pockets of muscovite and biotite are encountered.

The Gorodnitskoe and Koretskoe pegmatite fields of different zonal structure are located on the border of the Rovno and Zhitomir Oblast's: an aplite zone enriched with muscovite, biotite, often with garnet and tourmaline is located along the edges; the middle layer is coarse-grain pegmatite containing muscovite impurities and large tourmaline crystals; a quartz-feldspar zone is found in the central part, with predominance of feldspar.

The Gruzlivetskoe bed in the Zhitomir pegmatite field is being worked by the Dovbysh Porcelain Factory. Three veins of undifferentiated plagioclase-microcline pegmatites of pegmatoid, graphite, and garnet structures form the bed. As a result of the corresponding enrichment, the product satisfies the porcelain factory's requirements.

In the second half of the last century, searches for new kinds of raw material for the porcelain-faience industry began. Several types of Priazov'e garnets whose beds are located in the Zaporozhe and Donetsk Oblast's were the first to be recognized by specialists after traditional pegmatites. Samples of almost all potassium feldspar-containing garnets from the Ukraine shield were later comprehensively investigated. Leucocratic aplite-pegmatoid garnets and porphyritic granites of the Kirovograd and Novoukraine types found in the Kirovograd Oblast', coarse-grained Korosten'skoe granites from the Zhitomir Oblast', and medium-grain, weakly porphyritic Tokiv granites from the Dnepropetrovsk Oblast' were recognized as the most suitable for production of ceramic raw material that satisfies the requirements of industry. The materials obtained as a result of enrichment are characterized by a high feldspar content (35 – 40%) with predominance of potassium varieties and a minimal amount of inclusions of iron-containing minerals [1].

Nepheline syenites and albite-nepheline syenites and mariupolites whose basic beds are in Priazov'e (in Zaporozhe and the south of the Donetsk Oblast') could be a large-scale source of feldspar raw material in the very near future [5]. The nepheline-feldspar beds in this region consisting of alkaline rocks are complex rare-metal deposits (Zr, Nb, Ta), and in developing them, rare-metal-rare-earth concentrate is the basic product, while feldspar, nepheline, nepheline-feldspar, and other concentrates are associated.

Mazurovskoe and Kalino-Shevchenkovskoe beds, located in the Volnovakha region of Donetsk Oblast' are among the most investigated beds of this type; the average composition of the raw material of the indicated nepheline–feldspar deposits is (%): 19 – 20 Al_2O_3; 53 – 56 SiO_2; 10 – 14 K_2O + Na_2O; 3 – 5 Fe_2O_3 + FeO. Albite predominates among the feldspars [1]. Due to the high content of iron compounds, the rock must be concentrated. Concentrated nepheline syenite acts as a satisfactory flux (initial melting point of 940°C) and mullite-former. However, its melt is characterized by lower viscosity in comparison to the viscosity of a potassium feldspar melt. For this reason, articles made from pastes using nepheline syenites are less resistant to deformation during firing.

Industrial concentrations yttrium, tantalum, and niobium, as well as showings of scandium, strontium, cadmium, bismuth, etc.

The Donetsk Chemical Plant dumps formed as a result of zirconium mining, basically consisting of nepheline and feldspars (albite and microcline), are of special interest.

Arkosic sands and fine sands whose beds are located in the Dneprovsko-Donetsk basin (passing over the territory of Chernigov, Sumy, Poltava, and Khar'kiv Oblast's) and Donbas (covering the Lugansk, Donetsk, and Dnepropetrovsk Oblast's), can be considered as complex quartz-feldspar raw material. The chemical composition of the arkosic sands from the Nikolaevskoe showing (Donetsk Oblast') is as follows (%): 92.74 SiO_2; 3.19 Al_2O_3; 0.46 Fe_2O_3; 0.47 CaO; 0.21 MgO; 1.87 K_2O; 0.07 Na_2O [1].

In concentration of spodumene (in Priazov'e) and petalite (in Kirovgrad Oblast') pegmatites, spodumene concentrate containing 5.07% lithium oxide is obtained, with extraction of 88.5% and a yield of 18.8% of the initial ore. However, the main value of these pegmatites is the incidentally obtained quartz, feldspar, and sheet mica concentrates [6].

The studies in [7, 8] confirmed the possibility of utilizing lithium compounds to improve the properties of ceramics by enhancing mullite formation.

According to the data from the Ukraine Ministry of Ecology and Natural Resources, the Ukrainian shield lithium deposits are the largest in Europe. The ore-bearing showing deposits are considered as a new genetic type of rare-metal deposits for which a special name has been proposed — metapegmatites.

The lithium deposits located in Kirovograd (Polokhovskoe, Stankovatskoe) and in Donetsk (Shevchenkovskoe) regions are related to petalite–spodumene pegmatites and associated showings of Nb, Ta, and Cs. They are characterized by a high level of lithium concentration (up to 2% Li_2O). The following formations of rare-metal pegmatites are distinguished: microcline–albite–spodumene–petalite pegmatites containing columbite and chrysoberyl (Shevchenkovskoe deposit); albite–orthoclase–spodumene–petalite metapegmatites containing columbite and strüverite (Stankovatskoe deposit); petalite metapegmatites with columbite and chrysoberyl (Polokhovskoe deposit).

Concentration of lithium in petalite, which usually does not involve industrially important minerals in pegmatite deposits, is a special feature of lithium ore showings. Basic lithium aluminosilicate of ore from the Polokhovskoe deposit is represented by petalite, which contains 91 – 95% of the total amount of lithium in the ore. Its content in the rock is 27.6 – 32.6%. As the analysis in [9] showed, petalite from the Polokhovskoe deposit contains (%): 76.0 – 76.5 SiO_2; 17.1 – 17.3 Al_2O_3; < 0.1 Fe_2O_3; 3.9 – 4.7 Li_2O; 0.2 Na_2O; 0.2 K_2O; 0.005 Rb_2O. The possibility of obtaining petalite concentrate by different methods (flotation, flotation-gravity, gravity) was investigated. Having a density of 2.39 – 2.40 g/cm^3, petalite is the lightest ore mineral, which makes gravity concentration possible.

Alkaline feldspars, which consist of a total of 55 – 60% of the volume of the ore, are represented by albite and potassium feldspar (perthite). According to the findings of x-ray structural studies, high orthoclase and intermediate microcline were distinguished among the potassium phases of perthite based on the structural state.

Ukrainian mine samples vary in mineral composition, which allows prospecting for new, nontraditional (for Ukraine) sources of feldspar raw material already used in other countries. They include plagioclases, microclinites, plagioclase–microcline rocks, albites, feldspar metasomatites, as well as orthophyres, quartz–sercite orthoslates, and quartz porphyries. Special importance in this respect is attributed to the large amount of large- and giant-grain anorthosites, labradorite, and sterile albite from the Korosten'skoe (Zhiromir Oblast') and Korsyn'-Novomirgorodskoe (Kirovograd Oblast') showings.

Aplites — leucocratic medium- and fine-grain rock primarily consisting of feldspars (sodium, lime-sodium, potassium), and quartz are nontraditional types of feldspar raw material. Special attention is being focused on studies of aplite-pegmatoid granites which are close to pegmatites in composition and characterized by a high content of potassium and sodium oxides in the ratio of 2.0 – 2.5. The average composition of aplite-pegmatite granites from the Labunskoe deposit located in the Khmel'nitsky Oblast' is (%): 74.34 SiO_2; 114.95 Al_2O_3; 0.91 Fe_2O_3; 0.80 CaO; 038 MgO; 4.5 K_2O; 3.18 Na_2O; 1.48 K_2O : Na_2O; 7.70 $K_2O + Na_2O$ [1].

Deposits of plagioclasites consisting of plagioclase (oligoclase) and a small amount of quartz and biotite (for example, the Bazavlutskoe deposit located in the Nikopol' region of Dnepropetrovsk Oblast') have been explored in many regions in Ukraine.

Acid effusive rocks and the products of their alterations, orthophyres, quartz porphyries, quartz-sericite orthoslates, etc., are of some interest for expanding the raw materials base of ceramic materials. For example, the average composition of the orthophyres in the Kal'mius River basin is interesting (%): 15.38 K_2O; 0.24 Na_2O; 0.04 MgO; 0.40 CaO; 18.90 Al_2O_3; 64.19 SiO_2 [1].

Important rock deposits which are Neogenic intrusions of microgranodiorites and rhyolitic tuffs, are located southwest of the Ukrainian shield. Some of them, having undergone a hydrothermal effect, were transformed into kaolin rocks — porcelain stones. In Zakarpatskaya Oblast', liparites, keratophyres, kaolinized and alunitized tuffs from the Beregovskoe, Dubrinetskoe, and Vergel'skoe deposits should be considered as promising feldspar raw material, primarily of acid potassium feldspar composition.

Primarily granitic pegmatites, especially large-grain, ceramic, and leucocratic pegmatites containing microcline-perthite, and granitoid feldspar rocks, to which leucocratic microcline-albite granites belong, are the most important for ceramic production.

We should note that granitoid feldspar rocks have a number of advantages in comparison to pegmatites — the source

of this raw material for the porcelain-faience industry. First, they can be mined on wide scales by the open method. Second, the feldspar product obtained is characterized by homogeneous composition, is easily concentrated, and consequently is cheaper. Third, complex processing of some granites allows additionally obtaining a number of other valuable ore concentrates.

Kaolin concentration wastes, which are sands composed of quartz and feldspar, can be a second source for production of feldspar products. Since these sands, in contrast to pegmatite raw material, only contain potassium feldspar and almost no iron and other harmful components, the feldspar concentrate obtained will be of sufficiently high quality.

The third potential source of feldspar raw material is the separate layers of Upper Proterozoic arkosic (feldspar-quartz) sandstones. Laboratory-technical tests and technical-economic calculations demonstrated the expediency of removing feldspar concentrate from sandstones from the Bakhtinskoe deposit located in the Vinnitsa Oblast'. The reserves in fluorite ores are estimated at more than 3 million tons.

To increase the production volumes of high-potassium feldspar concentrates for the ceramics industry, it is expedient to also use other forms of mineral raw material such as nepheline syenites, metapegmatites from rare-metal lithium ore showings, and nontraditional kinds of feldspar raw material, aplites, plagioclasites, orthophyres, porcelain stones, etc., for example. Special attention should be focused on the problem of concentrating the mined raw material.

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